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(54) ALUMINA-BASED BODIES WITH LARGE PORES, PRODUCED BY AGGLOMERATION

(71) We, RHONE-PROGIL S.A., a French body corporate, of 25, Quai Paul Doumer, 92408 Courbevoie, France, do hereby declare the invention for which we pray that

a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention concerns very light alumina-based agglomerated bodies whose porosity comprises pores of large dimensions.

It is known that active aluminas have textural and structural properties which are related to the various methods of producing them, and that they can thus be put to very widely varying uses, for example in adsorption, chromatography and catalysis.

However, in most of the bodies which comprise active alumina, the porosity characteristics are related in particular to the specific surface area, so that bodies which have a large specific surface area have a relatively substantial porosity, but comprising pores of very small dimensions.

Now, it is often necessary to be able to produce active alumina bodies in which fine-pore porosity has superimposed thereon porosity comprising pores of substantially larger dimensions, in order to facilitate exchanges between the interior of such bodies and the media in which they are immersed; this obviously results in a much greater total pore volume, which means that these characteristics are difficult to achieve without a substantial reduction in mechanical strength, although this is a property which it is essential to safeguard in almost all the uses which can be envisaged.

A method which is well known amongst the various methods of producing active alumina bodies is that which comprises treating, in a stream of hot gas whose temperature can reach approximately 1000° C, hydrated aluminas, so as greatly to reduce their water content and thereby substantially change their crystalline

structure, bringing them, if necessary by crushing, to a suitable grain size, moistening them, agglomerating them by any known means, causing maturing of the agglomerated bodies thus produced, which causes them to harden by a setting phenomenon similar to that of hydraulic binding agents, and finally activating the resulting bodies, at temperatures which depend on the specific surface area to be imparted to such bodies; this method is described in particular in patent No. 754,008. The hydrated alumina most widely used in this process is aluminium α -trihydroxide or hydrargillite produced by the known Bayer method, which is crystalline in structure and which provides the aluminium industry with much of the alumina which it requires.

However, it is difficult to impart porosity comprising pores of large dimensions, to the agglomerated bodies which are produced from hydrargillite. Some methods however make it possible to achieve this aim, in particular by regulating the amount of moistening water and using a very restricted range of grain sizes; these methods are not without disadvantages, for example the industrial production of a restricted range of grain sizes is always a difficult problem to overcome, as is well known.

It has now been found that this method of dehydration by hot gas streams, when applied to alumina gels, makes it possible to produce agglomerated aluminous bodies which are highly porous, with pores of large dimensions, but which are nonetheless very strong.

Generally, it is known that hydrated alumina gels can be produced in various ways and from various compounds; however, on an industrial basis, the methods which are most generally used comprise precipitating alumina from alkali metal aluminates, in practice sodium aluminate, by acids, or alumina from various aluminium salts, by basic compounds. The pH range which permits precipitation of

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- the alumina extends approximately from 7.5 to 11; depending mainly on the selected pH conditions and temperature, it is possible to produce gels of varying compositions in which there is always an amorphous phase which exists virtually alone when precipitation occurs at temperatures which are close to ambient temperatures and at pH values which extend approximately from 8 to 9.
- Moreover, it is clear that continuous precipitation methods which permit conditions to be kept substantially constant are the most highly recommended for producing a substantially pure amorphous phase.
- It is also known that these gels evolve with time in the presence of a large excess of aqueous phase, such evolution being governed by the amount and the nature of the anions and cations present, temperature, and the presence of various crystalline seeds.
- Amorphous gels can be produced in the dry state only by very rapid drying operations. However, current practice involves drying in a drying oven at temperatures not much higher than 100° C in the presence of a large excess of water, as a result of which these gels evolve in a few hours towards boehmitic forms as can be seen from X-ray examination.
- However, although hydrargillite is converted by rapid dehydration in a stream of hot gases into complex substances comprising crystalline transition aluminas and a phase that is shown by X-ray analysis to be amorphous, which reagglomerate upon rehydration, it has now been discovered that gels subjected to the same process, which then do not have the time to evolve towards crystalline phases, give substances which from the crystallographic point of view have structures of low regularity and which can also be agglomerated by the absorption of water, an acid preferably being added to the water used. The agglomerated bodies which are produced in this way, after drying and activation by calcination, have porosity in which the largest pores arise from initially heated gels having the smallest amount of crystalline phase, and *vice versa*. In practice, the temperature of the gases, depending on the degree of dehydration desired and the nature of the substances to be treated, is from 350 to 1000° C, the residence times being suitably of the order of a second.
- This invention provides alumina bodies having macropores, formed by moistening and agglomerating alumina particles, in which at least a fraction of said particles is produced by dehydration in a stream of hot gas at a temperature of from 350° C to 1000° C, of a precipitated alumina gel which mainly comprises amorphous hydrated alumina, so that the particles have a residual amount of water, measurable by calcination at high temperature, of at least 8% by weight.
- Such a treatment, which is most easily carried out on small particles resulting from atomisation of aqueous suspensions of gels, can be continued until the amount of water which is contained in the resulting powdery substances and which can be measured by calcination at high temperature, is as little as 8% by weight, without such substances ceasing to have the property of giving solid agglomerated bodies after damping.
- It should be noted that this method is very different from that set out in U.K. Patent No. 1,129,980, in which totally amorphous alumina gels are dried at low temperature so that they still contain approximately 35% by weight of water, which substantially corresponds to their water constitution. Gels dried in this manner can be agglomerated after moistening, preferably by an ammoniacal solution, and the presence, in gels submitted to this drying operation, of well defined crystalline phases of alumina is not to be recommended because, since their crystalline structure cannot be modified at the low drying temperatures (not exceeding 200° C) used, they do not participate in the absorption of water and in the strength of the resulting agglomerates.
- In contrast, in the present method, all the crystalline phases which may be present are profoundly altered and participate in the strength of the agglomerates produced, the proportion of amorphous phase affecting only the number and size of pores of large dimensions.
- The gels which are treated in this way are in the form of highly porous spherical particles whose porosity, it is thought, is largely retained in the agglomerated bodies which are subsequently produced, which would be the reason for the high degree of porosity of the agglomerated bodies.
- It should be noted that the amount of water as measured by calcination at high temperature in the treated gels is at least 8% and can reach substantially that amount measured on gels which are simply dried, that is to say, approximately 35%; this loss by calcination can be increased as the amount of amorphous phase contained in the gels increases. In practice however, as on an industrial basis the treated gels contain other crystalline phases, losses which are measured by calcination at from approximately 8% to 25% by weight are the most attractive and correspond to a relatively high degree of crystallographic disorientation in the crystalline phases which may be present, which disorientation can be obtained only by the treatment with gases at relatively high temperatures.
- Owing to the agglomerating properties of the alumina gels treated in this way, it is possible to add particular bodies of substantially any nature whatever, and in particular particles of aluminas of various crystalline varieties, which may or may not be treated in hot gas streams, as well as particles of zeolites

or molecular sieves. In addition, these agglomerated bodies can comprise elements or compounds having catalytic effects of different natures, and in particular oxides and metals which are added, or whose precursors have been added, before or after the heat treatment in a gas flow, after the formation of the agglomerated bodies, or even to the sodium aluminate in order to coprecipitate them with the alumina.

It is possible also to modify the pore characteristics of the agglomerated bodies in accordance with previously known methods, for example carrying out hydro-thermal treatments, controlling the amount of agglomerating water and/or the range of grain sizes, and adding particles of various shapes which can disappear after agglomeration, by such means as decomposition, vaporisation, dissolution, combustion and calcination. Clearly the amount of these various additives must be such that the strength of the substances produced is not excessively reduced.

Various examples are given hereinafter in order to illustrate the present invention, these examples concerning agglomerates in the form of balls, which are produced in a rotary granulator, the last two examples being comparative examples: one concerns balls produced from a gel which is dried by atomisation at a low temperature and the other relates to balls which are produced from a gel which is calcined in an oven until it contains an amount of water, which can be measured by calcination at higher temperature, comprised within the preferred range mentioned above. These two examples are given in order clearly to show the specificity of the rapid action of hot gases on the nature of the results obtained. The results in all the examples, concerning balls which are calcined at 700° C and then at 1000° C, are summarised in the accompanying table which also gives the pore characteristics of the balls, their specific surface area in sq.m/g, their resistance to grain-by-grain crushing in kg, which is an average over 10 balls, and their resistance to attrition which is expressed in percent by weight of the balls which remains after wear by agitation for five minutes in a micro-crusher.

Obviously these examples are not limiting and in particular other general methods of agglomerating particulate substances can be used with similar results, such as agglomeration by compression and agglomeration by extrusion.

EXAMPLE 1.

A solution of sodium aluminate having 100 g/l of alumina expressed as Al_2O_3 is precipitated, in a continuous process at a pH maintained at 8.7 and at a temperature of 35° C, by a normal nitric acid solution.

The alumina gel suspension which issues from the reaction vessel then passes, for the

purposes of homogenisation, into a buffer tank which is also maintained at a temperature of 35° C, from which it is passed over a continuous filter. The resulting cake which comprises aluminium hydroxide which is virtually amorphous in respect of X-rays is washed with deionised water until the ions in the filtrate disappear, and then drained. The drained cake is then re-suspended by stirring in the deionised water so that it can be sprayed by means of a nozzle at the base of an apparatus for dehydration by a rising stream of hot gases produced by the burning of propane. The inlet temperature of the gases is 550° C, their outlet temperature is 300° C, and the contact time is about one second. The resulting powder, which is separated from the gases in a cyclone separator, has a water loss measured by calcination at high temperature of 24%, and a bulk density of 0.30 g/ccm; it is formed of substantially spherical particles having a diameter of less than 100 microns, 70% of such particles having a diameter of less than 44 microns. This powder is moistened by means of an aqueous N/2 nitric acid solution and agglomerated to the form of balls in a rotary granulator; the balls produced are then kept in a closed vat for a period of 8 hours at a temperature of 30° C, dried in a gas flow at 200° C and then calcined for two hours at 700° C; the balls are then sifted so as to retain only those whose diameters are from 2.4 to 4 mm. A fraction of these sifted balls is then calcined for 24 hours at 1000° C.

EXAMPLE 2.

An alumina gel cake is prepared in a similar manner to the mode of operation described in Example 1, although the pH-value in this case is maintained at around 8.0 and the temperature is maintained at about 30° C. The suspension issuing from the precipitation reaction vessel passes into the buffer tank at 30° C, before being passed over the filter. The cake which is also substantially amorphous is washed, re-suspended, treated in the hot gas flow and converted into balls, in the manner described in Example 1. The balls produced in this manner are dried, graded and calcined in the same manner.

EXAMPLE 3.

Balls are prepared in a rotary granulator as set out in Example 1, but after agglomeration and before drying, the balls are subjected to a hydro-thermal treatment for five hours at 100° C in a saturating vapour. The balls are then treated as in Example 1. The vapour treatment of the crude balls makes it possible to increase the strength of the balls, by reducing their pore volume.

EXAMPLE 4.

A mixture is made which contains by weight 50% of the same powder as that pro-

duced in Example 1, and 50% of a 5 Å molecular sieve of mono-crystals of from 2 to 5 microns diameter. This mixture is agglomerated in a rotary granulator after moistening with a N/2 nitric acid solution. The balls produced are subjected to a hydrothermal treatment for five hours at 100° C in a closed vessel. Calcination at 700° C for a period of 2 hours is then effected.

EXAMPLE 5.

A powder having the formula $2\text{CuO} \cdot 1 \text{Cr}_2\text{O}_3$ is prepared by calcination at 400° C of an intimate mixture of cupric nitrate and chromic anhydride. This powder is mixed with the alumina powder produced as set out in Example 1, in a proportion of 18% by weight of oxides with respect to the alumina. Agglomeration is effected, followed by maturing and calcination under the same conditions as in Example 1. By virtue of its macro-porosity, this catalyst has a high degree of activity as regards the oxidation of carbon monoxide and the hydrocarbons present in very substantial gas flows, e.g. the exhaust gases of engines. It also has a degree of stability which is higher than that of catalysts containing the same oxides deposited by impregnation.

EXAMPLE 6.

This example is given by way of compari-

son and relates to a gel which is dried at moderate temperature. An alumina cake is prepared as set out in Example 1. This cake is re-suspended and then dried in an atomiser in which the inlet temperature of the gases is 180° C and the outlet temperature is 80° C. The powder which is collected, which is virtually amorphous, has a water loss as measured by calcination at high temperature of 40% by weight, and a bulk density of 0.85 g/ccm which is much higher than that of the powder of Example 1. This powder is converted into balls in a rotary granulator and the balls are then treated in the same manner as in Example 1.

EXAMPLE 7.

This example is also given by way of comparison and concerns a gel which is calcined in an oven. The same alumina cake as that of Example 1 is dried in a drying oven, coarsely crushed and calcined in an oven at 500° C so that the loss by calcination at high temperature of this cake is 10% by weight. It is then crushed into the form of powder having particles which are smaller than 100 microns. This powder has a bulk density of 0.65 g/ccm and is agglomerated in the form of balls in a rotary granulator as in Example 1. The balls produced are treated in an identical manner.

TABLE

Balls calcined at 700°C	EXAMPLES						
	1	2	3	4	5	6	7
Total pore volume ccm/g	1.15	1.11	0.85	0.50	0.95	0.60	0.65
Macroporous volume (pores of diameter >0.05 micron) ccm/g	0.47	0.43	0.20	0.10	0.35	0.14	0.15
Specific surface area sq.m/g	250	230	220	410	190	250	300
Mean resistance to crushing kg	4.5	4.0	6.0	3.0	3.0	7.0	8
Resistance to attrition %	99.8	99.8	99.6	98	98	99.5	99

Balls calcined at 700°C then 1000°C	EXAMPLES						
	1	2	3	4	5	6	7
Total pore volume ccm/g	1.08	1.00	0.80	—	0.85	0.58	0.60
Specific surface area sq.m/g	120	95	110	—	85	95	100
Mean resistance to crushing kg	3.0	3.1	4.0	—	2.3	6.2	7
Resistance to attrition %	99.7	99.5	99.7	—	97	99.3	99

5 This table clearly shows that, in spite of their large pore volume, all the alumina agglomerates have a good mechanical strength, particularly as regards attrition, and that even the agglomerates which are half composed of molecular sieves (Example 4) still have levels of strength which are sufficient for them to be employed in industrial uses. This table also shows by comparison between the results of Examples 6 and 7, and the results of Examples 1, 2 and 3, that the large pore volumes are obtained solely by using gels which are dehydrated rapidly in a stream of hot gases.

15 WHAT WE CLAIM IS:—

1. Alumina bodies having macropores, formed by moistening and agglomerating alumina particles, wherein at least a fraction of said particles is produced by dehydration in a stream of hot gas at a temperature of from 350° C to 1000° C, of a precipitated alumina gel that mainly comprises amorphous hydrated alumina, so that the particles have a residual amount of water, measurable by calcination at high temperature, of at least 8% by weight.

2. Bodies according to claim 1, wherein the amount of water which can be measured by calcination at high temperature is from 8 to 35% by weight.

3. Bodies according to claim 1, wherein the amount of water which can be measured by calcination at high temperature is from 8 to 25% by weight.

4. Bodies according to any one of claims 1 to 3, wherein the gel subjected to dehydration contains a crystalline variety of hydrated alumina.

5. Bodies according to any one of claims 1 to 4, wherein one or more other components are added to the dehydrated alumina particles.

6. Bodies according to claim 5, wherein the said other components are particulate and selected from hydrated aluminas which have been treated in a stream of hot gases, zeolites, molecular sieves, oxides and metals.

7. Bodies according to claim 5, wherein the said other component(s) have a catalytic action.

8. Bodies according to claim 5, wherein the said other component(s) are removed upon calcination.

9. Bodies according to claim 1, substantially as hereinbefore described with reference to any of Examples 1 to 5.

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